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METAL ALKOXIDES - MODELS FOR METAL OXIDES

by

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Bloomington, IN 47405

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Metal Alkoxides - Models for Metal Oxides

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In the spirit of this symposium, I should like to invite discussion of my proposal that metal alkoxides (1) may act as models for metal oxides in their reactions with a wide variety of hydrocarbons and small unsaturated molecules. Since metal oxides provide the most versatile class of heterogeneous catalysts used in the petrochemical industry, studies of metal alkoxides, which are hydrocarbon soluble, could shed light on metal oxide catalyzed reactions and furthermore might yield a new generation of homogeneous catalysts. The fact that metal oxide catalysts are effective for reactions such as olefin-hydrogenation, -isomerization, -polymerization and -metathesis implies that metal-hydrogen and metal-carbon bonds are involved, perhaps in an analogous manner to those which are well documented in organometallic chemistry (2). This by itself is an interesting thought since metal oxides seem far removed from the now classical organometallic compounds which abound with ligands such as tertiary phosphines, carbonyls,  $\pi$ -bonded cyclopentadienes and arenes, etc. How can a metal-oxide environment compete with the sophisticated ligand systems that the contemporary organometallic chemist has available for catalyst design? Apparently, metal-oxide systems compete very effectively and certainly in some instances there are no known homogeneous analogues. One can think of CO/H<sub>2</sub> activation in Fischer-Tropsch chemistry as just one system in which the metal oxide catalysts win hands down over homogeneous metal-carbonyl chemistry (3). Let us speculate what special requirements a metal oxide environment or surface may provide. Factors which come to my mind include (i) unusual coordination numbers, geometries and electronic configurations for metal atoms; (ii) oxo ligands are strong  $\pi$ -donors, which contrast with most ligands commonly used in organometallic chemistry which are  $\pi$ -acceptors; (iii) oxo ligands may act as terminal six-electron ( $M=O$ ) or four-electron ( $M=O$ ) ligands (4) or may act as bridging ( $\mu_2$ -,  $\mu_3$ -,  $\mu_4$ -,  $\mu_5$ - and  $\mu_6$ -) ligands and changes from one form to another may readily occur in response to the addition or elimination of

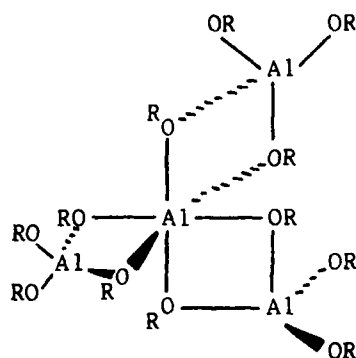
substrate molecules; and (iv) for many transition elements in their lower, middle and even penultimate oxidation states, metal-metal bonding may be important. Of course, in mixed metal oxide systems, there can be important contributions from two or more different metal atoms acting collectively to bring about activation that would not be possible in a homometallic system. The idea of heterobimetallic activation of small but "tough" molecules such as CO has gained much attention in homogeneous organometallic chemistry within the last few years (3) and in view of the mixed metal nature of many oxide catalysts it would seem equally important in heterogeneous systems.

Let us first examine some of the structural and electronic relationships that exist for metal oxides and metal alkoxides.

#### Structural and Electronic Analogies between Metal-Oxides and Alkoxides

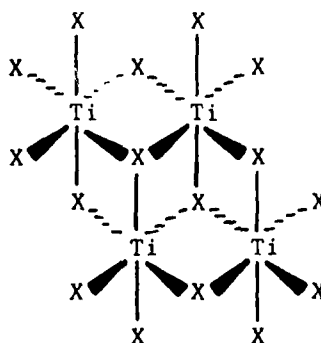
I shall take the simple view that most metal oxide structures are derivatives of a closest packed  $O^{2-}$  lattice with the metal ions occupying tetrahedral or octahedral holes in a manner which is principally determined by size, charge (and hence stoichiometry) and  $d^n$  configuration (5). The presence of d electrons can lead to pronounced crystal field effects or metal-metal bonding. The latter can lead to clustering of metal atoms within the lattice with large distortions from idealized (ionic) geometries.

In 1958, Bradley (6) proposed a structural theory for metal alkoxides  $M(OR)_n$  based on the desire of metal ions to achieve their preferred coordination number and geometry by oligomerization involving the formation of alkoxide bridges ( $\mu_2$  or  $\mu_3$ ). For compounds of formula MOR, octahedral and tetrahedral geometries are not attainable, but the cubane-like  $M_4(OR)_4$  structure which affords the maximum coordination number, 3, is often found, e.g.  $M = Ti$  and  $Na$  (1). For  $M(OR)_2$  compounds, a tetrahedral geometry is possible for a tetramer and an octahedral geometry can be envisaged for an infinite polymer. For  $M(OR)_3$  compounds, tetrahedral geometries and octahedral geometries are easily obtained by oligomerization. One structural characterization of  $Al(O-i-Pr)_3$  reveals a central octahedrally coordinated  $Al(III)$  ion surrounded by three tetrahedral  $Al(III)$  ions. (See I below.)  $Cr(O-i-Pr)_3$ , on the other hand, only exists in a polymeric form which is totally insoluble in hydrocarbon solvents. Based on spectroscopic and magnetic data,  $[Cr(O-i-Pr)_3]_n$  is believed to have  $Cr(III)$  in only octahedral environments.<sup>n</sup> The difference between  $Al(III)$  and  $Cr(III)$  is interesting and is readily understandable when one recognizes the marked propensity for the  $d^3$  ion to adopt octahedral geometries to the exclusion of others - a fact which is generally reconciled with crystal field stabilization energies (5).



I

The structure of  $[\text{Ti}(\text{OEt})_6]_4$ , reported by Ibers (7) in 1963 was of historic significance since it provided the first structural test of Bradley's theory for a compound of formula  $\text{M}(\text{OR})_6$ . Each titanium atom achieves an octahedral environment, through the agency of four doubly bridging and two triply bridging alkoxy groups, as is shown in II.



II

Compounds of formula  $\text{M}(\text{OR})_3$  can readily attain an octahedral geometry by dimerization to give two edge-sharing octahedra  $[\text{M}(\mu_2\text{-OR})(\text{OR})_4]_2$  and this has been verified by the structural characterization of  $[\text{Nb}(\text{OMe})_5]_2$  (1).

In 1967, Bradley (8) wrote further about metal oxide-alkoxide (trialkylsiloxide) polymers. He noted that these compounds  $[\text{MO}^x(\text{OR})^{y-2x}]_n$  are interesting polymeric compounds which bridge the gap between the oligomeric alkoxides  $[\text{M}(\text{OR})_3]_m$  and the macromolecular metal oxides  $[\text{M}_2\text{O}]_a$ . Similarly, the metal oxide trialkylsilyloxides  $[\text{MO}(\text{OSiR}_3)^y]_n$  may be regarded as intermediate between the oligomeric metal trialkylsilyloxides  $[\text{M}(\text{OSiR}_3)_3]_m$  and the mineral silicate macromolecules.

The central  $\text{Ti}_2\text{O}_4$  unit in  $\text{Ti}_2\text{O}_4(\text{OEt})_{10}$  (9), and the  $\text{Nb}_2\text{O}_4$  unit in  $\text{Nb}_2\text{O}_4(\text{OEt})_{10}$  (10) are shown in Figure 1 and reveal a striking similarity to both the  $[\text{Ti}(\text{OEt})_6]_4$  structure and the structures of isopoly and heteropolyacids of molybdenum, tungsten and vanadium.

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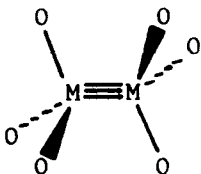
Recently some interesting analogies have been found between metal-oxides and alkoxides where the  $d^n$  configuration is important in leading to strong metal-metal bonds. For example, the  $[\text{Ti}(\text{OEt})_4]_4$  type of structure involving four fused octahedra to give a centrosymmetric  $M_4$  rhomboheral unit is also found for  $W_4(\text{OR})_{16}$ , where  $R = \text{Me}$  or  $\text{Et}$  (11,12). Here the eight electrons from the  $W(4+)$  ions are used in cluster bonding. The same basic geometry is found in the mixed alkoxy-oxo molybdenum compound  $\text{Mo}_4(=\text{O})_4(\mu_2-\text{O})_2(\mu_3-\text{O})_2(\mu_2-\text{O}-i\text{-Pr})_2(\text{O}-i\text{-Pr})_2(\text{py})_4$  (12) and in ternary metal oxides  $\text{Ag}_8\text{W}_4\text{O}_{16}$  (13) and  $\text{Ba}_{11}\text{Mo}_8\text{O}_{16}$  (14). The structure of the latter is particularly interesting: (1) There are infinite chains of metal cluster units bound together in such a way that tunnels are constructed for the  $\text{Ba}^{2+}$  ions. (2) The clusters are of two types, though both have the connectivity  $\text{Mo}_4\text{O}_2\text{O}_8/2\text{O}_6/3$ . Both share the basic  $M_4X_{16}$  geometry found in  $M_4(\text{OEt})_{16}$  ( $M = \text{Ti}$  and  $\text{W}$ ), but differ with respect to M-M distances. In one cluster unit, there are roughly five equally short Mo-Mo distances, 2.58 Å (averaged), while in the other there are two longer Mo-Mo distances, 2.85 Å (averaged). In keeping with the stoichiometry  $\text{Ba}_{11}\text{Mo}_8\text{O}_{16}$ , it is reasonable to assign the regular and elongated clusters as having ten and eight cluster bonding electrons, respectively. A particularly interesting comparison of M-M distances in these  $M_4X_{16}$  containing units can be made as a function of the number of cluster bonding electrons 0, 4, 8 and 10. See Table I. Cotton and Fang (15) recently carried out calculations which suggested that the lengthening of two M-M bonds in the eight electron cluster  $W_4(\text{OEt})_{16}$  results from a 2nd order Jahn-Teller distortion which accompanies removal of two electrons from the regular  $C_{2h}$  rhomboheral  $M_4$  geometry. The latter accommodates ten cluster electrons in effectively five M-M bonds. McCarley (14) notes in describing the  $\text{Mo}_4$  clusters found in  $\text{Ba}_{11}\text{Mo}_8\text{O}_{16}$  that these were metal-metal bonded adaptations of the well known hollandite structure and closely related to the cluster found for  $\text{CsNb}_4\text{Cl}_{11}$ .

Triangulo  $\text{Mo}_3$  and  $\text{W}_3$  units are common in discrete coordination clusters (16) and ternary oxides (19,20,21) and may accommodate five, six, seven and eight cluster bonding electrons (12). In the mixed oxo alkoxides of formula  $\text{Mo}_3(\text{O})(\text{OR})_{10}$ , where  $R = \text{CH}_2-t\text{-Bu}$  and  $i\text{-Pr}$ , the Mo-Mo distance is 2.535 Å (averaged) (23), which may be compared with  $\text{Mo-Mo} = 2.524(2)$  Å (averaged) in  $\text{Zn}_2\text{Mo}_3\text{O}_8$  (19,20). The coordination about the molybdenum atoms is similar, but not the same for these triangulo complexes as is shown in Figure 2. In both cases, the molybdenum atoms are surrounded by six oxygen ligands in a distorted octahedral manner. One can imagine that the  $\text{Mo}_3(\mu_3-\text{O})(\mu_3-\text{OR})(\mu_2-\text{OR})_2(\text{OR})_4$  structure could be converted to the  $\text{Mo}_3(\mu_3-\text{O})(\mu_2-\text{O})_2(\text{O})_3$  structure by a reaction in which the  $\mu_3-\text{OR}$  ligand becomes a terminal OR group to one molybdenum and two new terminal bonds are formed, one to each of the other two molybdenum atoms. This has

not yet been achieved chemically, but a hypothetical reaction is easily envisaged:  $\text{Mo}_3(\mu_3\text{-X})_2(\mu_2\text{-X})_3(\text{X})_6 + 2\text{X} \rightarrow \text{Mo}_3(\mu_3\text{-X})-(\mu_2\text{-X})_3(\text{X})_9$ . Thus, the  $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu_2\text{-OR})_3(\text{OR})_6$  structure may be viewed as coordinatively unsaturated with respect to that found in the presence of a single capping ( $\mu_3$ ) ligand.

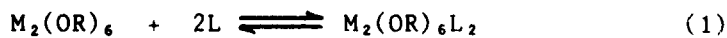
M-M multiple bonding has long been known in metal oxide structures. The first Mo=Mo bond was seen in one crystalline form of  $\text{MoO}_2$  which has a distorted rutile structure wherein the  $\text{Mo}(4+)$  ions occupy adjacent octahedral holes throughout the lattice (24). The octahedra are distorted because of the short Mo-Mo distances 2.51 Å.  $\text{La}_4\text{Re}_2\text{O}_{10}$  has a fluorite type structure in which  $\text{O}^{2-}$  is substituted for  $\text{F}^-$  and four of the five  $\text{Ca}^{2+}$  sites are occupied by  $\text{La}^{3+}$  ions. The remaining  $\text{Ca}^{2+}$  site is occupied by an  $(\text{Re}=\text{Re})^{8+}$  unit with an Re-Re distance 2.259(1) Å (25).

In the alkoxides  $\text{M}_2(\text{OR})_6$ , where  $\text{M} = \text{Mo}$  and  $\text{R} = \text{t-Bu}$ ,  $\text{i-Pr}$  and  $\text{CH}_2\text{-t-Bu}$  and  $\text{M} = \text{W}$  and  $\text{R} = \text{t-Bu}$ , there are unbridged  $\text{M}=\text{M}$  bonds (26). The  $\text{Mo}_2\text{O}_6$  geometry has approximate  $\text{D}_{3d}$  symmetry, as shown in III below, and in this way a  $\text{Mo}_2^{6+}$  unit occupies a distorted  $\text{O}_6$  octahedral cavity.



III

The compounds  $\text{M}_2(\text{OR})_6$  ( $\text{M}=\text{M}$ ), where  $\text{M} = \text{Mo}$  and  $\text{W}$ , are coordinatively unsaturated and react reversibly with donor ligands such as amines (27,28) and phosphines (29) according to eq. 1. The position of equilibrium appears to be largely determined by steric factors associated with  $\text{R}$  and  $\text{L}$ .



In the solid state, the  $\text{M}_2(\text{OR})_6\text{L}_2$  compounds have four coordinated metal atoms united by  $\text{M}=\text{M}$  bonds. The four ligands coordinated to each metal atom lie roughly in a square plane as is shown in Figure 3.

I shall mention just two further alkoxide structures which I believe are noteworthy with respect to metal oxide structures. The first is  $\text{W}_4(\mu\text{-H})_2(\text{O-i-Pr})_{14}$  (30) whose central  $\text{W}_4\text{H}_2\text{O}_{14}$  skeleton is shown in Figure 4. This molecule may be viewed as a dimer of  $\text{W}_2(\mu\text{-H})(\text{O-i-Pr})_7$ . The average oxidation state of tungsten is +4 and evidently the eight electrons available for M-M bonding are used to form two localized double bonds:  $\text{W}(1)\text{-W}(2) = \text{W}(1')\text{-W}(2') = 2.45$  Å and  $\text{W}(1)\text{-W}(1') = 3.41$  Å. This may be viewed as a model for a section of a reduced tungsten oxide. Through the agency of bridging oxygens and

hydrides, tungsten attains an octahedral environment and the  $d^n$  electrons are used to form metal-metal bonds. Formally, the outer tungsten atoms are in oxidation state  $+4\frac{1}{2}$ , while the inner ones are  $+3\frac{1}{2}$ .

The structure of the centrosymmetric molecule  $\text{Mo}_6\text{O}_{10}(\text{O}-i\text{-Pr})_{12}$  (31) has an S-chain of six molybdenum atoms and is shown in Figure 5. Here there are both six and five coordinate molybdenum atoms and terminal and bridging oxo and alkoxide ligands. The average oxidation state for molybdenum is 5.33 which leaves four electrons available for metal-metal bonding. These are evidently used to form two localized single Mo-Mo bonds (2.585(1) Å). An interesting feature not previously seen in metal alkoxide structures is the presence of "semi-bridging" RO ligands. One of the alkoxy ligands on each of the six-coordinate terminal molybdenum atoms is positioned beneath the basal plane of its five coordinate neighboring molybdenum atom. The Mo---O distance is 2.88(1) Å, much too long for a regular bridging distance, but much too short to be viewed as non-bonding. Furthermore, the regular Mo-OR bond is lengthened and the Mo-O-C angle of this terminal OR group indicates that there is significant interaction between the oxygen lone pair and the neighboring molybdenum atom. The structure suggests incipient bond formation. The facile interconversion of terminal and bridging ligands (O and OR) is a dominant feature of the chemistry of these compounds. In solution,  $\text{W}_4(\mu\text{-H})_2(\text{O}-i\text{-Pr})_{14}$  and  $\text{Mo}_6\text{O}_{10}(\text{O}-i\text{-Pr})_{12}$  are fluxional on the nmr time-scale and both molecules are coordinatively unsaturated.

#### Oxygen-to-Metal $\pi$ -Bonding

Certain general trends in M-O bond distances can be correlated with bond multiplicity and the degree of oxygen-to-metal  $\pi$ -bonding. A comparison of M-O bond distances for structurally related compounds having a  $\text{M}_4(\mu_3\text{-X})_2(\mu_2\text{-X})_4\text{X}_{10}$  unit is given in Table II. For M = Mo and W in closely related compounds, differences in M-L distance are negligible.

1. The terminal M-O distances follow the order  $\text{Ba}_{1.14}\text{Mo}_8\text{O}_{16} > \text{RO-M}$  in both  $\text{W}_4(\text{OEt})_{16}$  and  $\text{Mo}_4\text{O}_8(\text{O}-i\text{-Pr})_4(\text{py})_4 > \text{Ag}_8\text{W}_4\text{O}_{16} > \text{O}=\text{Mo}$  in  $\text{Mo}_4\text{O}_8(\text{O}-i\text{-Pr})_4(\text{py})_4$ . This trend is readily understood in terms of the relative degrees of O-to-M  $\pi$ -bonding in the series and places terminal RO ligands somewhere between the infinite chain oxygen donor ligands found in the ternary molybdenum oxide and the terminal oxo ligands found in  $\text{Ag}_8\text{W}_4\text{O}_{16}$ , which approximates to  $\text{W}_4\text{O}_{16}^{8-}$ , with weak coordination to Ag ions.

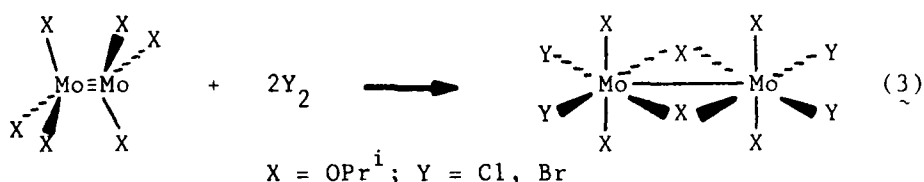
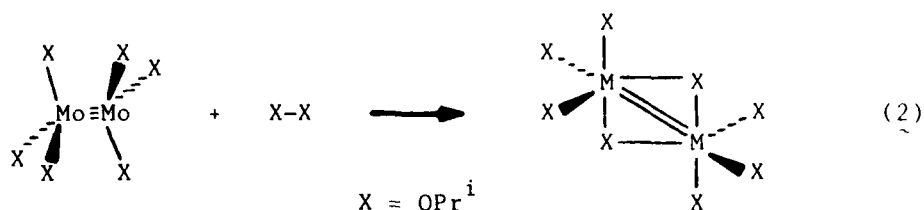
2.  $\text{M}-\mu_2\text{-O}$  and  $\text{M}-\mu_3\text{-O}$  distances are slightly shorter for oxo ligands than for alkoxy ligands. This general observation may, however, be masked by other factors. For example, the  $\text{M}-\mu_3\text{-O}$  distances in  $\text{Ag}_8\text{W}_4\text{O}_{16}$  and  $\text{W}_4(\text{OEt})_{16}$  are comparable but longer than those in McCarley's compounds. These deviations

from the general rule,  $d_{M-\mu-OR} > d_{M-\mu-O}$ , may be accounted for by considerations of trans influences (32) operating within the octahedral units. The triply bridging oxo groups in  $Ag_8W_4O_{16}$  are trans to terminal W-O bonds which are short (1.79 Å average) because of multiple bond character. An examination of the three Mo- $\mu_3$ -O distances in  $Mo_4O_8(O-i-Pr)_4(py)_4$  is particularly informative since the bonds are trans to three different ligands, namely oxo, isopropoxy and pyridine, which have different trans influences. A similar large asymmetry occurs in the M- $\mu_2$ -O distances in  $Ag_8W_4O_{16}$  and  $Mo_4O_8(O-i-Pr)_4(py)_4$  and may be traced to the different trans influences of terminal oxo and bridging oxo ligands.

What influence will strong  $\pi$ -donor ligands have in organometallic chemistry? This question is one which cannot be answered reliably at this time. The stabilization of unusual coordination numbers and geometries by  $\pi$ -donor ligands in compounds such as  $Mo(O-t-Bu)_2(py)_2(CO)_2$  and  $Mo(CO)_2(S_2CNR_2)_2$  has attracted the attention of Hoffmann (33) and Templeton (34) and their coworkers. We have noted that RO  $\pi$ -donors may produce anomalous properties in other ligands which are coordinated to the same metal. For example, in  $Mo(CO)_2(O-t-Bu)_2(py)_2$  (35), the carbonyl stretching frequencies are anomalously low for carbonyl groups bonded to Mo(2+),  $\nu(CO) = 1906$  and  $1776\text{ cm}^{-1}$  and, in  $Mo(O-i-Pr)_2(bpy)_2$ , the 2,2'-bipyridyl ligands appear partially reduced from X-ray and Raman studies (36). Qualitatively, both of these observations may be rationalized in terms of RO-to-M  $\pi$ -bonding. Strong  $\pi$ -donor ligands raise the energy of the  $t_{2g}$  electrons and, thus, enhance metal backbonding to  $\pi^*$ -acceptor ligands, even to ligands such as 2,2'-bipyridine which do not usually behave as  $\pi$ -acceptor ligands in the ground state in transition metal coordination compounds.

#### Reactions of Metal-Metal Bonded Alkoxides of Molybdenum and Tungsten

Having established structural and electronic analogies between metal oxides and alkoxides of molybdenum and tungsten, the key remaining feature to be examined is the reactivity patterns of the metal-alkoxides. Metal-metal bonds provide both a source and a returning place for electrons in oxidative-addition and reductive elimination reactions. Stepwise transformations of M-M bond order, from 3 to 4 (37,38), 3 to 2 and 1 (39) have now been documented. The alkoxides  $M_2(OR)_6$  ( $M=Mo$ ) are coordinatively unsaturated, as is evident from their facile reversible reactions with donor ligands, eq. 1, and are readily oxidized in addition reactions of the type shown in equations 2 (39) and 3 (39).



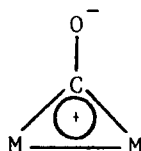
Upon oxidation, alkoxy bridges seem to be invariably formed and this may be viewed as an internal Lewis base association reaction in response to the increased Lewis acidity of the metal ions which accompanies the changes  $(\text{M} \equiv \text{M})^{6+} \rightarrow (\text{M} = \text{M})^{8+} \rightarrow (\text{M} - \text{M})^{10+}$ . The structural changes which take the ethane-like  $\text{X}_3\text{M} \equiv \text{MX}_3$  unit to two fused trigonal bipyramids, sharing a common equatorial-axial edge, to two face- or edge-shared octahedra are fascinating.

The  $\text{M}_2(\text{OR})_6$  compounds provide a good source of electrons to ligands that are capable of being reduced upon coordination. For example,  $\text{Ph}_2\text{CN}_2$ , reacts with  $\text{Mo}_2(\text{O-i-Pr})_6$  in the presence of pyridine to give the adduct  $\text{Mo}_2(\text{O-i-Pr})_6(\text{N}_2\text{CPh}_2)_2(\text{py})_2$  (40) in which the diphenyldiazomethane ligand may be viewed as a  $2e^-$  ligand,  $\text{Mo} = \text{N} = \text{N} = \text{CPh}_2$ , and the dimolybdenum unit may be viewed as  $(\text{Mo} - \text{Mo})^{10+}$ . See Figure 6.

The four electrons involved in the two Mo-Mo bonds in  $\text{Mo}_6\text{O}_{10}(\text{O-i-Pr})_{12}$  (Figure 5) are reactive to molecular oxygen:  $\text{Mo}_6\text{O}_{10}(\text{O-i-Pr})_{12} + \text{O}_2 \rightarrow 6/n[\text{MoO}_2(\text{O-i-Pr})_2]_n$ . The structure of  $[\text{MoO}_2(\text{O-i-Pr})_2]_n$  is not presently known, but the 2,2'-bipyridine (bpy) adduct  $\text{MoO}_2(\text{O-i-Pr})_2(\text{bpy})$ , which is obtained by addition of bpy to a hydrocarbon solution of  $[\text{MoO}_2(\text{O-i-Pr})_2]_n$  has been structurally characterized and shown to have the expected octahedral geometry with cis di-oxo ligands (41).

Carbon monoxide reacts with  $\text{M}_2(\text{OR})_6$  compounds and the first step has been shown to involve the reversible formation of  $\text{M}_2(\text{OR})_6(\mu\text{-CO})$ . A structural characterization of  $\text{Mo}_2(\text{O-t-Bu})_6(\mu\text{-CO})$  reveals an interesting square based pyramidal geometry for each molybdenum atom (42). See Figure 7. The two halves of the molecule are joined by a common apical bridging CO ligand, a pair of basal bridging OR ligands and formally a Mo=Mo bond. Closely related compounds  $\text{M}_2(\text{OR})_6\text{L}_2(\mu\text{-CO})$  have been isolated for  $\text{R} = \text{i-Pr}$  and  $\text{CH}_2\text{-t-Bu}$  where L is a donor ligand such as an amine (43). The structures of the  $\text{M}_2(\text{O-i-Pr})_6(\text{py})_2(\mu\text{-CO})$  compounds ( $\text{M} = \text{Mo}, \text{W}$ ) have been determined by X-ray studies and

reveal a similarity to the  $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  structure: the pyridine ligands complete the confacial bioctahedral geometry by forming bonds trans to the M-C bonds. Characteristic features of these compounds are their exceedingly low values of  $\nu(\text{CO})$ , ca. 1650 (Mo) and 1550  $\text{cm}^{-1}$  (W) and low carbonyl carbon chemical shifts, ca. 325 ppm (Mo) and 315 ppm (W) downfield from  $\text{Me}_4\text{Si}$ . These low values, which are unprecedented for neutral bridging ( $\mu_2$ -) carbonyl compounds, imply a great reduction in C-O bond order. In a formal sense, the  $\text{Mo}_2(\text{OR})_6(\mu\text{-CO})\text{(py)}_2$  compounds are inorganic analogues of cyclopropenones and it is possible to envisage a significant contribution from the resonance form IV, shown below, which emphasizes the analogy with a bridging oxy alkylidyne ligand. Bridging alkylidyne carbon resonances in  $[(\text{Me}_3\text{SiCH}_2)_2\text{W}(\mu_2\text{-CSiMe}_3)]_2$  are found at 353 ppm (44).



IV

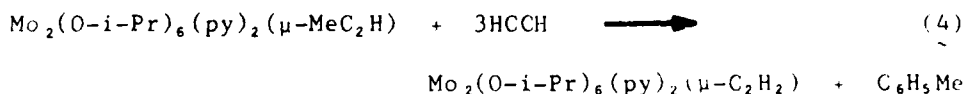
$\text{Mo}_2(\text{OR})_6$  compounds in hydrocarbon solvents rapidly polymerize acetylene to a black metallic-looking form of polyacetylene. Propyne is polymerized to a yellow powder, while but-2-yne yields a gelatinous rubber-like material (45). The detailed nature of these polymers is not yet known and the only molybdenum containing compounds recovered from these polymerization reactions were the  $\text{Mo}_2(\text{OR})_6$  compounds. When the reactions were carried out in the presence of pyridine/hexane solvent mixtures, simple adducts  $\text{Mo}_2(\text{OR})_6(\text{py})_2(\text{ac})$  were isolated for  $\text{R} = i\text{-Pr}$  and  $\text{CH}_2-t\text{-Bu}$ , and  $\text{ac} = \text{HCCH}$ ,  $\text{MeCCH}$  and  $\text{MeCCMe}$  (45,46).

The structure of  $\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  is shown in Figure 8. The central  $\text{M}_2\text{C}_2$  unit is typical of those commonly found in dinuclear organometallic complexes, e.g.  $\text{Co}_2(\text{CO})_8(\text{RCCR})$  (47),  $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{HCCH})$  where  $\text{M} = \text{Mo}$  (48) and  $\text{W}$  (49) and  $(\text{COD})_2\text{Ni}_2(\text{RCCR})$  (50). The acetylenic C-C distance (1.368(6) Å) in the  $\text{Mo}_2(\text{OR})_6(\text{py})_2(\text{HCCH})$  compound is slightly longer than that in ethylene, 1.337(3) Å (51). The acetylenic distance in  $\text{W}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\text{HCCH})$ , which is isostructural with the molybdenum compound, is even longer, 1.413(19) Å. Again, we see the ability of the  $\text{M}_2(\text{OR})_6$  compounds to donate electron density to  $\pi$ -acceptor ligands with the order  $\text{W} > \text{Mo}$ . In a formal sense, this can be viewed as an oxidative-addition reaction accompanied, as usual, by a return to octahedral geometries through the agency of alkoxy bridges and, in this instance, a bridging alkyne ligand.

The neopentoxy compound  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ , which can be prepared by the addition of one equivalent of acetylene to  $\text{Mo}_2(\text{ONE})_6(\text{py})_2$ , reacts further with another equivalent of acety-

lene to yield  $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$  (45,46). An ORTEP view of this interesting molecule is shown in Figure 9. The formation of a  $\text{M}_2(\mu\text{-C}_4\text{R}_4)$  unit by the coupling of two acetylenes at a dimetal center is a well recognized feature of organometallic chemistry and was first seen in 1961 with the structural characterization of  $(\text{CO})_6\text{Fe}_2(\mu\text{-C}_4\text{Me}_2(\text{OH})_2)$ , a product obtained from the reaction between but-2-yne and alkaline solutions of ironhydroxycarbonyl:  $\text{MeCCMe}\cdot\text{H}_2\text{Fe}_2(\text{CO})_6$  (53). In  $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$ , one molybdenum atom is incorporated in a metalla-cyclopentadiene ring, while the other is  $\pi$ -bonded to the diene in a  $\eta^4$ -manner. Formally, one molybdenum is in oxidation state  $+4\frac{1}{2}$  and the other  $+3\frac{1}{2}$ . In any event, the dimolybdenum center has been oxidized from  $(\text{Mo}\equiv\text{Mo})^{6+}$  to  $(\text{Mo}=\text{Mo})^{8+}$  and we see a return to the confacial bioctahedral geometry in which the  $\mu\text{-C}_4\text{H}_4$  ligand occupies two sites of the bridging face.

These  $\mu\text{-C}_2\text{R}_2$  and  $\mu\text{-C}_4\text{H}_4$  molybdenum alkoxides are very soluble in hydrocarbon solvents which allows their characterization in solution by  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectroscopy. In all cases, low temperature limiting spectra have been obtained which are consistent with those expected based on the structures found in the solid state. It is also possible, by nmr studies, to elucidate their role in alkyne oligomerization reactions and all available evidence indicates that they are not active in polymerization, but are active in cyclotrimerization which yields benzenes. For example, when  $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$  was allowed to react with ca. 20 equiv. of  $\text{C}_2\text{D}_2$  in a sealed nmr tube, the  $^1\text{H}$  intensity of the signal arising from the  $\mu\text{-C}_4\text{H}_4$  ligand decreased as a signal due to  $\text{C}_6\text{H}_4\text{D}_2$  grew. Similarly, when  $\text{Mo}_2(\text{O-i-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  was allowed to react with ca. 20 equiv. of  $\text{C}_2\text{D}_2$ , a benzene proton resonance appeared and, within the limits of  $^1\text{H}$  nmr integration, the intensity of this signal corresponded to the loss of the  $\mu\text{-C}_2\text{H}_2$  signal. When  $\text{Mo}_2(\text{O-i-Pr})_6(\text{py})_2(\mu\text{-MeCCH})$  was allowed to react with  $\text{HCCH}$ , ca. 20 equiv., formation of toluene was observed along with  $\text{Mo}(\text{O-i-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  and the ratio of the  $\mu\text{-C}_2\text{H}_2$  and toluene- $\text{CH}_3$  signals was 2:3, which establishes the stoichiometry of the reaction shown in eq. 4.



The species responsible for alkyne polymerization, which is kinetically more facile than cyclotrimerization since only a small fraction of the added alkyne is converted to benzenes, is not yet known. Carbene-metal complexes, both mononuclear (54) and binuclear ( $\mu_2\text{-CR}_2$ ) complexes (55,56), have been shown to act as alkyne polymerization initiators and several years ago it was shown that terminal alkynes and alcohols can react to give alkoxycarbene ligands (57). As yet, we have no evidence

that carbene ligands are formed in these reactions, but they remain high on the list of possibly active species present in these reactions.

$W_4(\mu-H)_2(O-i-Pr)_{14}$  (30) is one of the very few transition metal hydrido alkoxides that have been claimed in the literature (58,59). It is the only one to be fully structurally characterized by an X-ray study and, though in the solid state each tungsten is in a distorted octahedral environment (Figure 4), it behaves in solution as a coordinatively unsaturated molecule. It is fluxional on the  $^1H$  nmr time-scale in toluene- $d_8$ . Even at the lowest temperatures accessible in that solvent there is one time averaged type of O-i-Pr group and a hydride resonance at  $\delta = 7.87$  ppm flanked by tungsten satellites of roughly one-fifth intensity due to coupling to  $^{183}W$  which has  $I = \frac{1}{2}$  and 14.4% natural abundance. The appearance of only one coupling constant,  $J_{183W-1H} = 96$  Hz, and the intensity of the satellites indicate that the hydride ligand sees two equivalent (time-averaged) tungsten atoms. Cryoscopic molecular weight determinations in benzene gave  $M = 1480 \pm 80$ , which showed that the tetranuclear nature of the complex is largely or totally maintained in non-coordinating solvents. However, in p-dioxane, the molecular weight was close to half the value obtained in benzene, which suggests that the tetranuclear complex is cleaved in donor solvents to give solvated  $W_2(\mu-H)(O-i-Pr)_7$ . In the mass spectrometer, a very weak molecular ion was detectable, but the major ion, by field desorption, was  $W_2(\mu-H)(O-i-Pr)_7^+$ . All of this is consistent with the view that cleavage of one or both of the central alkoxy bridges, which are long (and weak) being trans to the hydrido ligand and span the  $W(1)$  to  $W(1)'$  atoms which are non-bonded ( $W(1)-W(1)'$  3.407(1) Å), creates a vacant coordination site. This molecule thus provides an interesting opportunity for the study of the reactivity of the bridging hydrido ligand. In a quick survey of its reactions with unsaturated hydrocarbons carried out in nmr tubes in toluene- $d_8$  solution, it has been found (30) to react rapidly with ethylene, allene and diphenyl acetylene. In each case, the  $W\mu$ -hydride resonance was lost. The reaction with ethylene is evidently reversible since attempts to isolate the presumed ethyl complex formed by insertion yield only  $W_4(\mu-H)(O-i-Pr)_{14}$ . Moreover, when  $W_4(\mu-H)_2(O-i-Pr)_{14}$  was allowed to react with a large excess of  $CH_2=CD_2$  in an nmr tube, the labels in the excess ethylene were rapidly scrambled and when  $W_4(\mu-D)_2(O-i-Pr)_{14}$  was reacted with excess  $CH_2=CH_2$ , the  $W_4(\mu-H)_2(O-i-Pr)_{14}$  compound was recovered.  $W_4(\mu-H)_2(O-i-Pr)_{14}$  and 1-butene show no apparent reaction at room temperature in toluene- $d_8$ , but at 60°C, 1-butene is selectively isomerized to cis 2-butene (60).

#### Concluding Remarks

1. The structural analogies between metal oxides, metal-alkoxides and metal-alkoxide-oxide polymers originally noted for  $d^0$  metal systems can be extended to metal-metal bonded systems.

2. Metal-metal bonds in molybdenum and tungsten alkoxides provide a ready source of electrons for oxidative-addition reactions and addition reactions involving  $\pi$ -acidic ligands.

3. The structural properties and chemical reactivities of the  $M_2-\mu-C_2R_2$ ,  $-\mu-C_4H_4$ ,  $-\mu-H$  groups have direct parallels with those of "classical" organometallic compounds.

4. The catalytic cycles that have been documented, namely alkyne cyclotrimerization and olefin isomerization, demonstrate that addition and elimination from dimetal centers can occur readily in the presence of metal-metal bonds and alkoxide ligands.

5. Alkoxide ligands, which are strong  $\pi$ -donors and may readily interchange terminal and bridging ( $\mu_2$  or  $\mu_3$ ) bonding sites, could play an important role in the future development of organometallic chemistry, particularly that of the early transition elements which may wish to increase their coordination numbers and valence shell electron configurations. Alkoxides of titanium, so-called organic titanates, in the presence of aluminum alkyls or alkylaluminum halides, have already been used for polymerization and copolymerization reactions of olefins and dienes, but this has attracted little mechanistic attention. Schrock and his coworkers (61) have shown that alkoxide ligands may be used to suppress  $\beta$ -hydrogen elimination reactions in olefin metathesis reactions involving niobium and tantalum catalysts.

Finally, I should like to draw attention to the work of others who have provided models for metal oxides and their interactions with hydrocarbon and organometallic fragments. Specifically the work of Klemperer (62,63,64) and Knoth (65,66,-67) and their coworkers have provided us with discrete salts of the heteropolyanions to which a variety of organic/organometallic fragments have been adhered.

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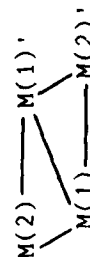
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Table I. M-M Distances (Å) Found in Compounds which are Structurally Related to  $W_6(OEt)_{16}$ .<sup>a</sup>

Compound	M(2)-M(1)'	M(1)-M(2)	M(1)-M(1)'	Number of $M_n$ Cluster Electrons	Ref.
$[Ti(OEt)_4]_6$	3.34	3.50	3.42	0	b
$Ag_8W_4O_{16}$	3.32	3.23	3.49	0	c
$Mo_4O_8(OPr^i)_4(py)_4$	3.47	2.60	3.22	4	d
$W_6(OEt)_{16}$	2.65	2.94	2.76	8	d
$Ba_{1.14}Mo_8O_{16}$	2.54	2.84	2.56	8	e
$Ba_{1.14}Mo_8O_{16}$	2.61	2.57	2.58	10	e

(a) Distances are quoted to  $\pm 0.01$  Å; the labelling scheme for  $M(1)$ ,  $M(2)$  and  $M(1)'$  is shown below and is such that  $M(1)$  and  $M(2)$  have, respectively, two and three terminal groups. (b) Ibers, J.A. Nature 1963, 197, 686. (c) Skarstad, P.M.; Geller, S. Mat. Res. Bull. 1975, 10, 791. (d) Ref. 12. (e) McCarley, R.E.; Luly, M.H.; Ryan, T.R.; Torardi, C.C. ACS Symp. Series 1981, 155, 41.



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Table II. Comparison of Metal-to-Oxygen Bond Distances ( $\text{\AA}$ )  
in Compounds which are Structurally Related to  $W_4(\text{OEt})_{16}$ .<sup>a</sup>

Compound	M-O Terminal	M-O $\mu_2$	M-O $\mu_3$
$W_4(\text{OEt})_{16}$ <sup>b</sup>	1.96 1.90 1.94 1.93 1.98	2.03 2.02 2.08 2.03	2.17 2.16 2.20
$Ag_8W_4O_{16}$ <sup>c</sup>	1.80 1.73 1.77 1.79 1.83	1.86 2.20 1.87 2.14	2.11 2.15 2.22
$Mo_4O_8(\text{OPr}^i)_4(\text{py})_4$ <sup>b</sup>	1.68 (=O) 1.70 (=O) 1.94 (OR)	1.95 (-O-) 1.94 (-O-) 2.12 (OR) 2.24 (OR)	1.98 2.18 2.04
10 electron $Mo_4$ cluster in $Ba_{1.14}Mo_8O_{16}$ <sup>d</sup>	2.10, 2.08 2.21, 2.09 2.06, 1.99 2.11, 2.14 2.03, 2.06	2.05, 2.01 2.06, 2.05 1.93, 1.92 2.08, 1.95	2.06, 2.10 2.03, 2.07 2.03, 2.09
8 electron $Mo_4$ cluster in $Ba_{1.14}Mo_8O_{16}$ <sup>d</sup>	1.94, 1.85 2.06, 2.10 2.10, 2.12 2.09, 2.00 2.11, 2.14	1.94, 1.91 2.00, 1.99 2.10, 2.00 2.10, 2.04	2.05, 2.12 1.99, 2.12 1.99, 2.08

(a) Distances quoted to  $\pm 0.01 \text{ \AA}$ . (b) Ref. 12. (c) Skarstad, P.M.; Geller, S. Mat. Res. Bull. 1975, **10**, 791. (d) McCarley, R.E.; Luly, M.H.; Ryan, T.R.; Torardi, C.C. ACS Symp. Series 1981, **155**, 41.

### Captions to Figures

Figure 1. The  $\text{Ti}_7\text{O}_{24}$  unit in  $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$  and the  $\text{Nb}_8\text{O}_{30}$  unit in  $\text{Nb}_8\text{O}_{10}(\text{OEt})_{20}$ .

Figure 2. The  $\text{Mo}_3\text{O}_{13}$  unit found in  $\text{Zn}_2\text{Mo}_3\text{O}_8$  (top) and the  $\text{Mo}_3\text{O}(\text{OC})_{10}$  unit found in  $\text{Mo}_3\text{O}(\text{OR})_{10}$  compounds ( $\text{R} = \text{CHMe}_2$  and  $\text{CH}_2\text{CMe}_3$ ) (bottom).

Figure 3. Two stereo stick views of the  $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6(\text{py})_2$  molecule viewed perpendicular to the Mo-Mo bond (top) and down the Mo-Mo bond (bottom).

Figure 4. The central  $\text{W}_4(\mu\text{-H})_2\text{O}_{14}$  skeleton of the centrosymmetric  $\text{W}_4(\mu\text{-H})_2(\text{O-i-Pr})_{14}$  molecule emphasizing the octahedral geometries of the tungsten atoms.

Figure 5. ORTEP view of the centrosymmetric  $\text{Mo}_6\text{O}_{10}(\text{O-i-Pr})_{12}$  molecule. Some pertinent bond distances ( $\text{\AA}$ ) and angles (deg) are:  $\text{Mo}(1)\text{-Mo}(2) = \text{Mo}(1)'\text{-Mo}(2)' = 2.585(1)$ ,  $\text{Mo}(1)\text{-Mo}(1)' = 3.353(1)$ ,  $\text{Mo}(2)\text{-Mo}(3) = \text{Mo}(2)'\text{-Mo}(3)' = 3.285(1)$ ,  $\text{Mo}(1)'\text{-Mo}(1)\text{-Mo}(2) = 146.5(1)$ ,  $\text{Mo}(1)\text{-Mo}(2)\text{-Mo}(3) = 134.3(1)$ ; Mo-oxo (terminal) = 1.68 (averaged), Mo-oxo ( $\mu_2$ ) = 1.93 (averaged), Mo-OR (terminal) = 1.86 (average), Mo-OR ( $\mu_2$ ) = 2.05 to 2.19.

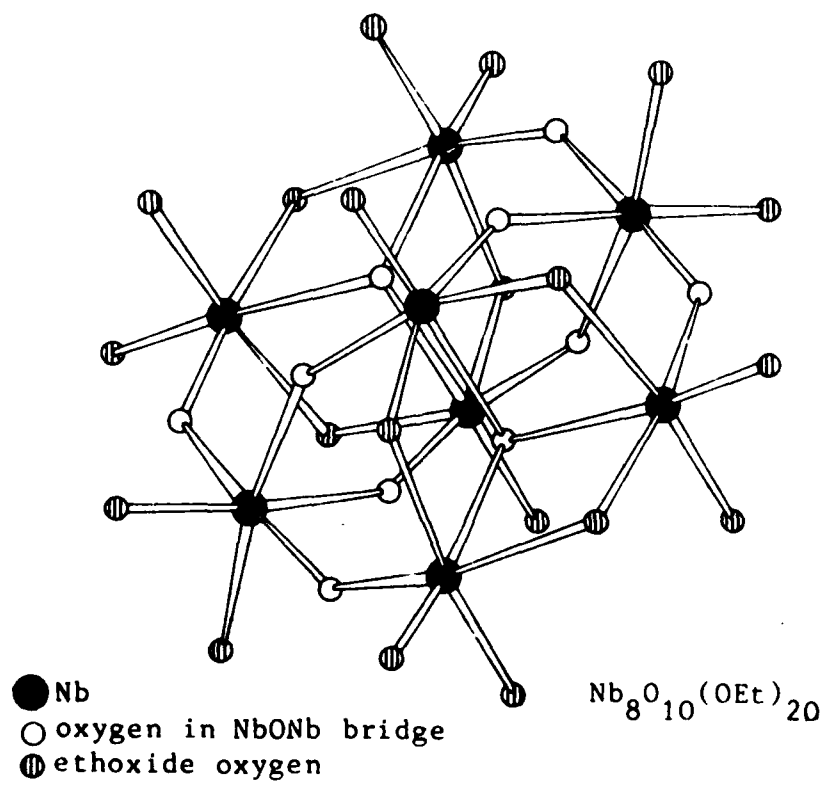
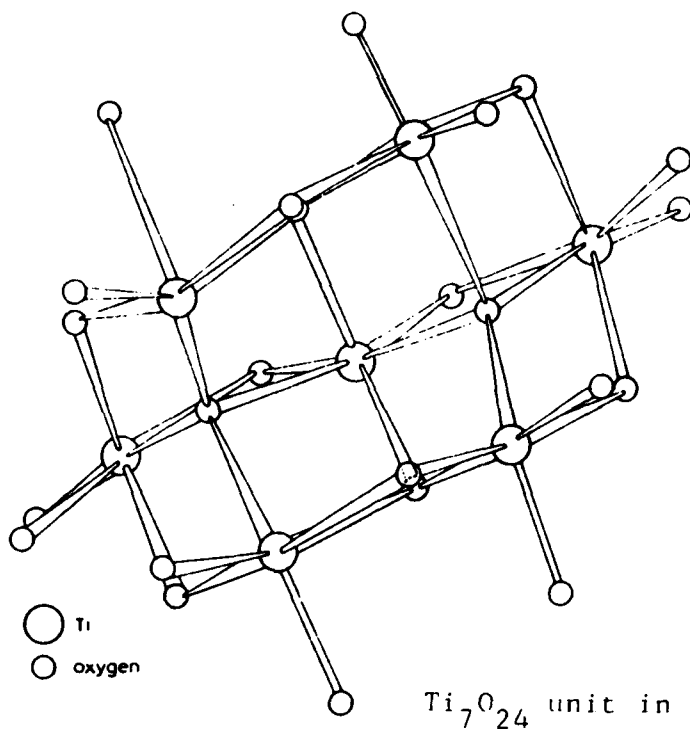
Figure 6. An ORTEP view of the  $\text{Mo}_2(\text{O-i-Pr})_6(\text{N}_2\text{CPh}_2)_2(\text{py})$  molecule. Some pertinent distances ( $\text{\AA}$ ) and angles (deg) are: Mo-Mo = 2.661(2);  $\text{Mo}(1)\text{-O}(39) = 1.96(1)$ ,  $\text{-O}(43) = 1.96(1)$ ,  $\text{-O}(47) = 2.24(1)$ ,  $\text{-O}(51) = 2.11(1)$ ,  $\text{-O}(55) = 2.13(1)$ ,  $\text{-N}(3) = 1.76(1)$ ;  $\text{Mo}(2)\text{-O}(47) = 2.16(1)$ ,  $\text{-O}(51) = 2.04(1)$ ,  $\text{-O}(55) = 2.04(1)$ ,  $\text{-O}(59) = 1.98(1)$ ,  $\text{-N}(18) = 1.78(1)$ ,  $\text{-N}(33) = 2.225(10)$ ;  $\text{N}(3)\text{-}$

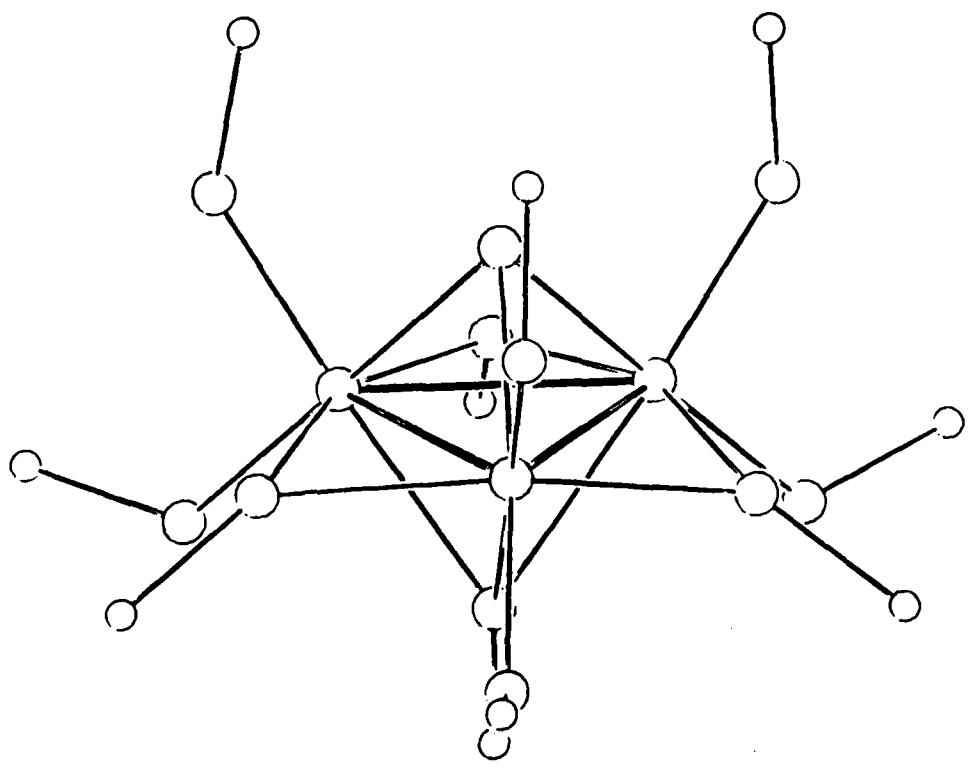
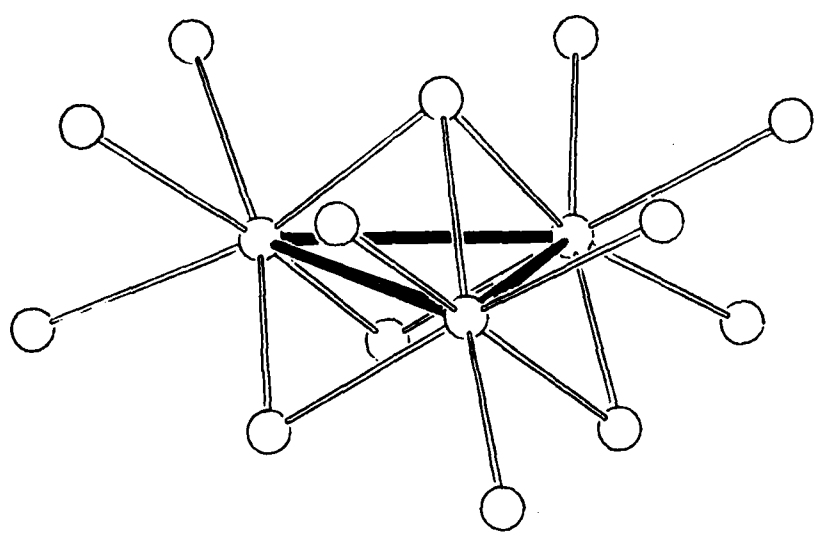
$N(4) = 1.30(1)$ ;  $N(4)-C(5) = 1.30(2)$ ;  $N(18)-N(19) = 1.30(1)$ ;  
 $N(19)-C(20) = 1.31(2)$ ;  $Mo(1)-N(3)-N(4) = 164(1)^{\circ}$ ;  $N(3)-N(4)-$   
 $C(5) = 124(1)^{\circ}$ ;  $Mo(2)-N(18)-N(19) = 155(1)^{\circ}$ ;  $N(18)-N(19)-C(20)$   
 $= 122(1)^{\circ}$ .

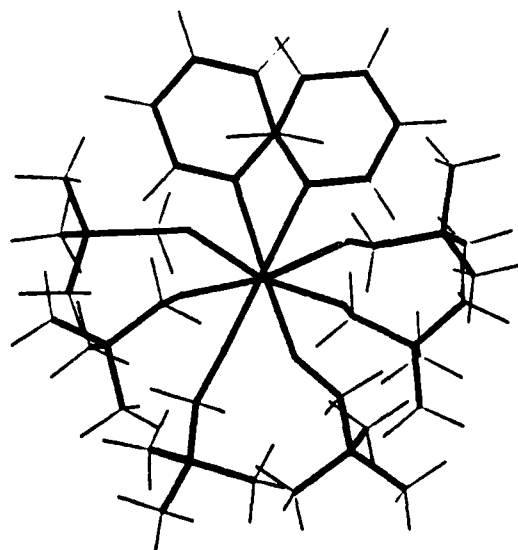
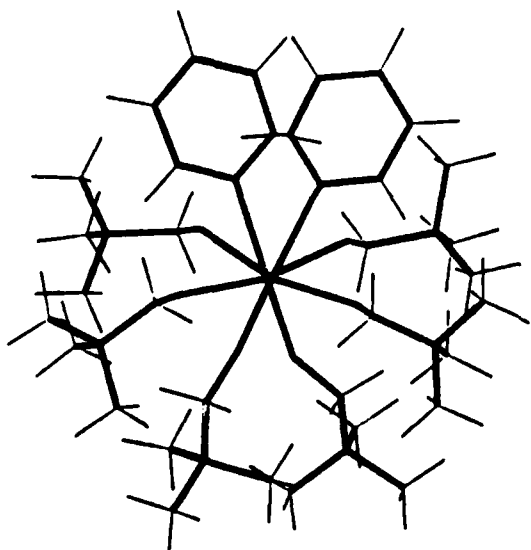
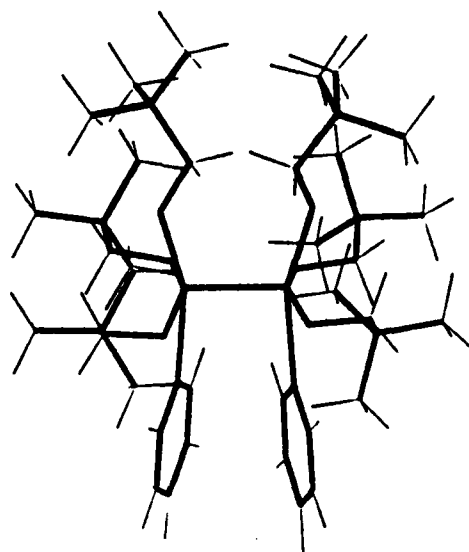
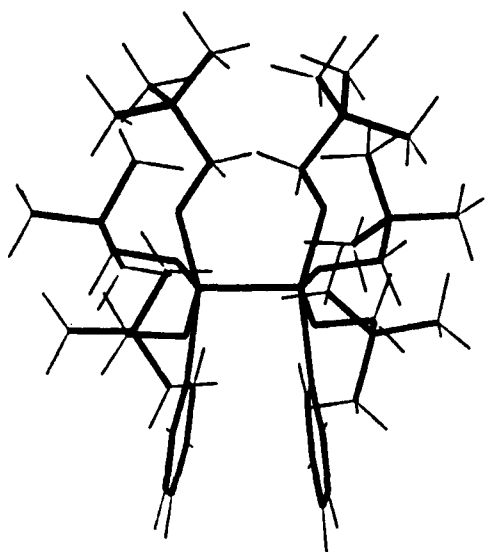
Figure 7. An ORTEP view of the central skeleton of the  $Mo_2(O-t-Bu)_6(\mu-CO)$  molecule.

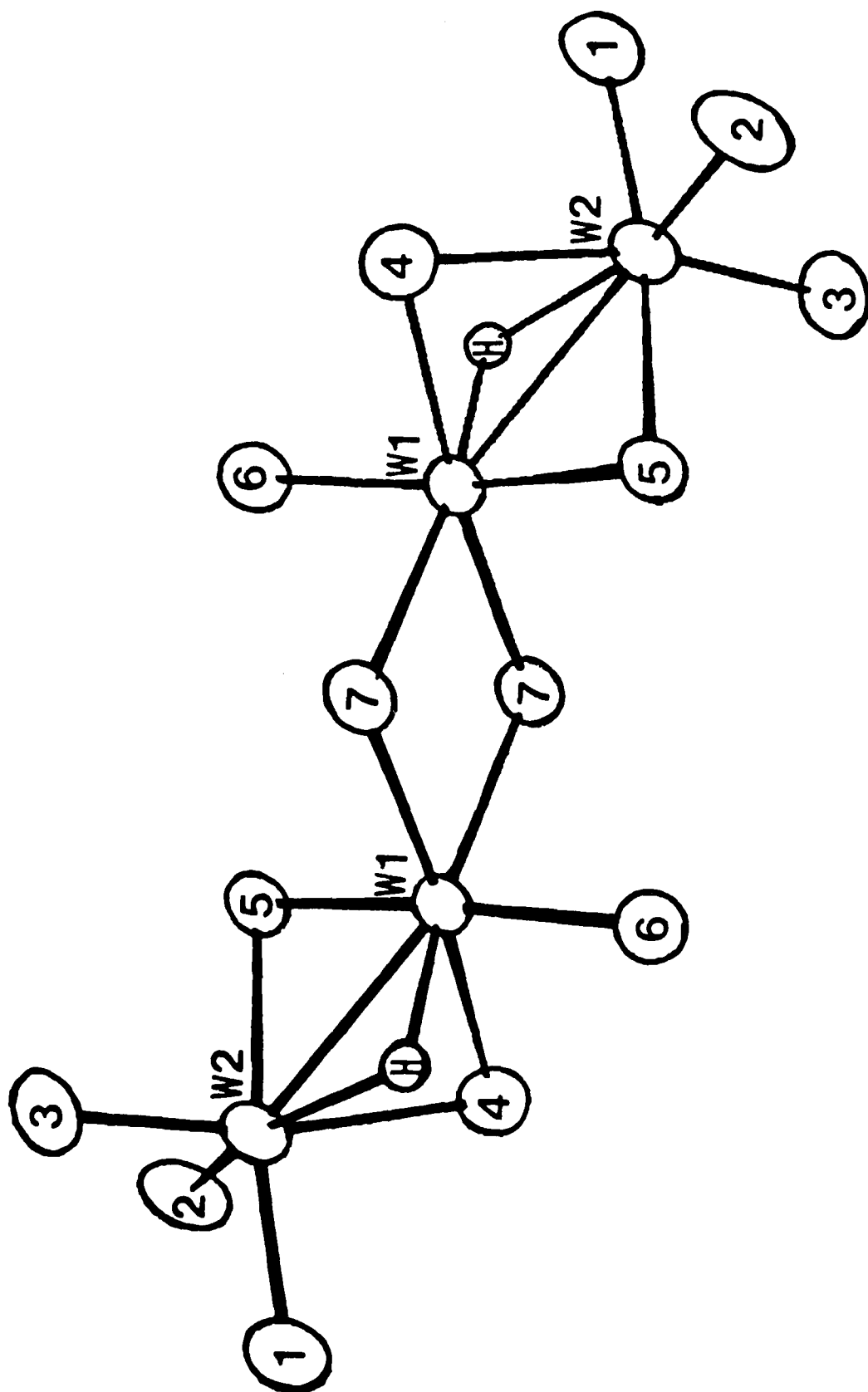
Figure 8. An ORTEP view of the  $Mo_2(O-i-Pr)_6(\mu-C_2H_2)(py)_2$  molecule. Pertinent bond distances ( $\text{\AA}$ ) are  $Mo(1)-Mo(2) = 2.554(1)$ ;  $Mo-O$  (terminal) = 1.94 (averaged),  $Mo-O (\mu_2) = 2.14$ ,  $Mo-N = 2.31$  (averaged),  $Mo-C = 2.09$  (averaged) and  $C-C (\mu\text{-acetylene}) = 1.368(6)$ .

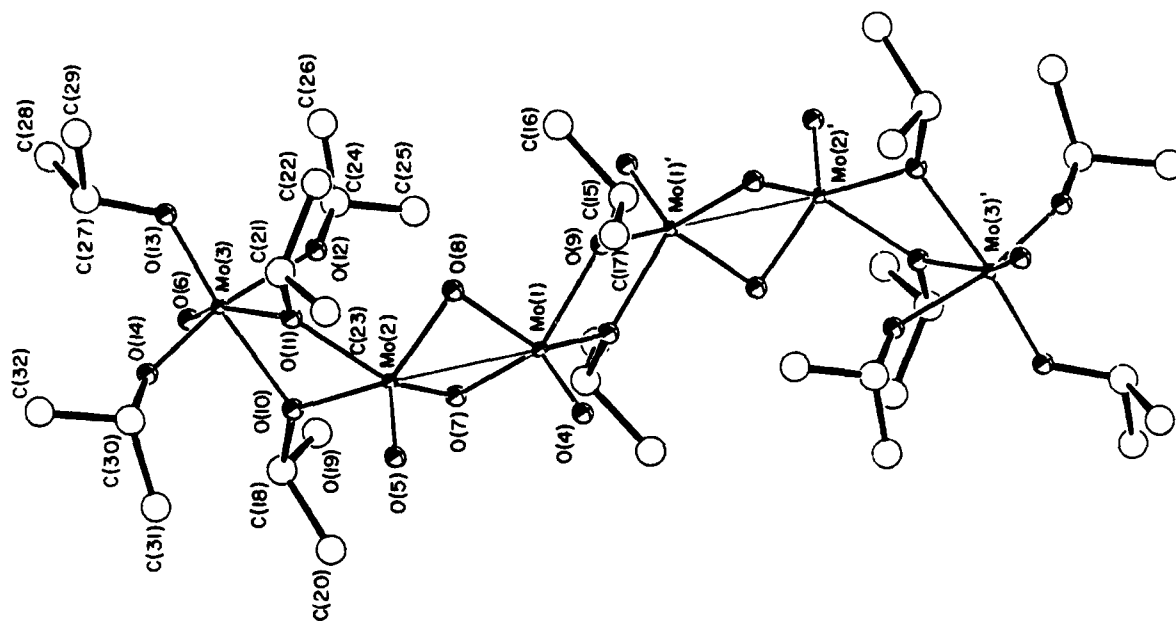
Figure 9. An ORTEP view of the  $Mo_2(ONe)_6(\mu-C_4H_4)(py)$  molecule. Some pertinent distances ( $\text{\AA}$ ) are:  $Mo(1)-Mo(2) = 2.69(1)$ ,  $Mo-O$  (terminal) = 1.92 (averaged),  $Mo-O (\mu_2) = 2.15$ ,  $Mo-N = 2.15(1)$ ,  $Mo(1)-C(3) = 2.12(2)$ ,  $Mo(2)-C(3) = 2.39(2)$ ,  $Mo(2)-C(4) = 2.34(2)$ ,  $C(3)-C(4) = 1.47(3)$ ,  $C(4)-C(4)' = 1.44(4)$ .

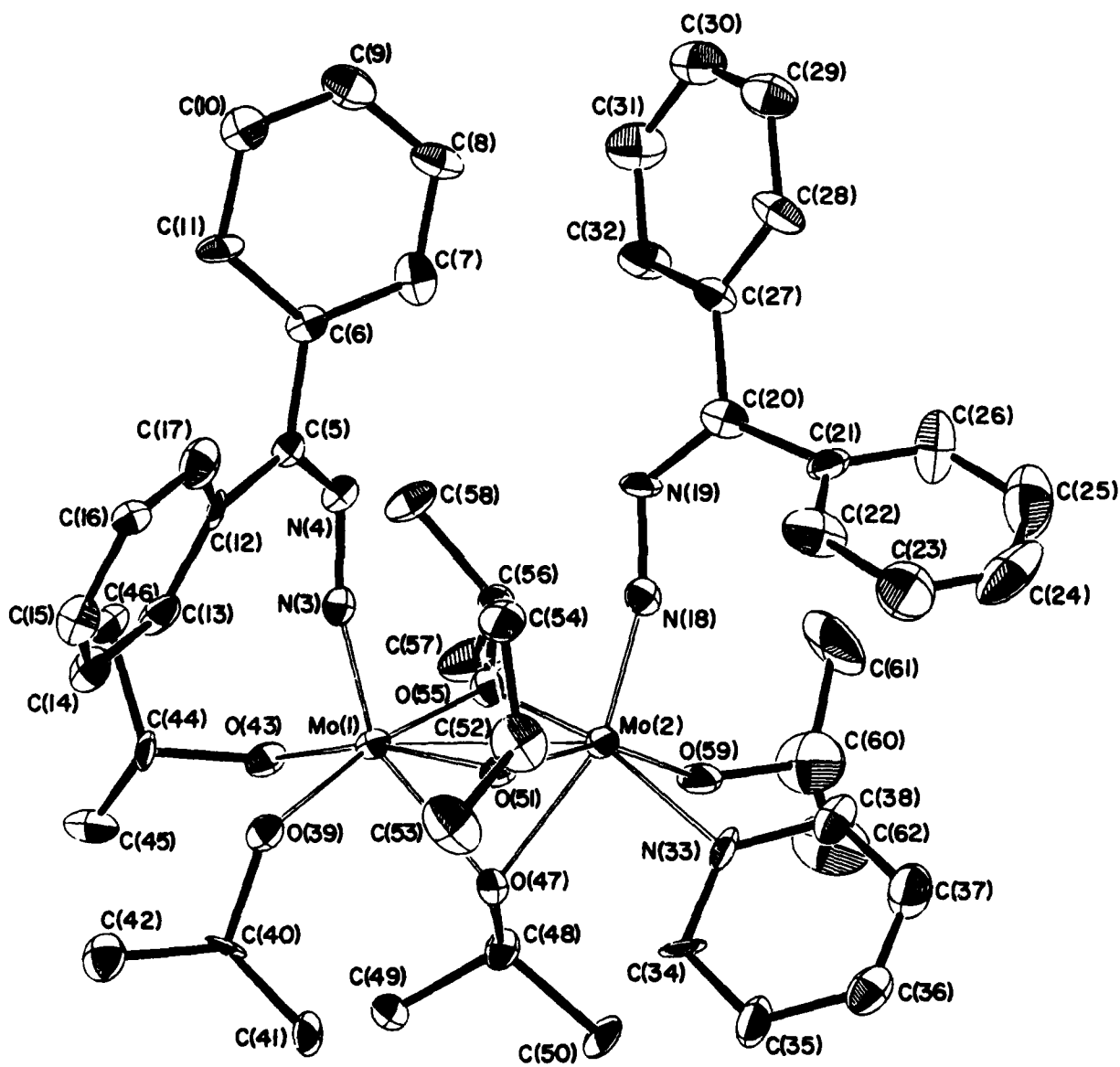


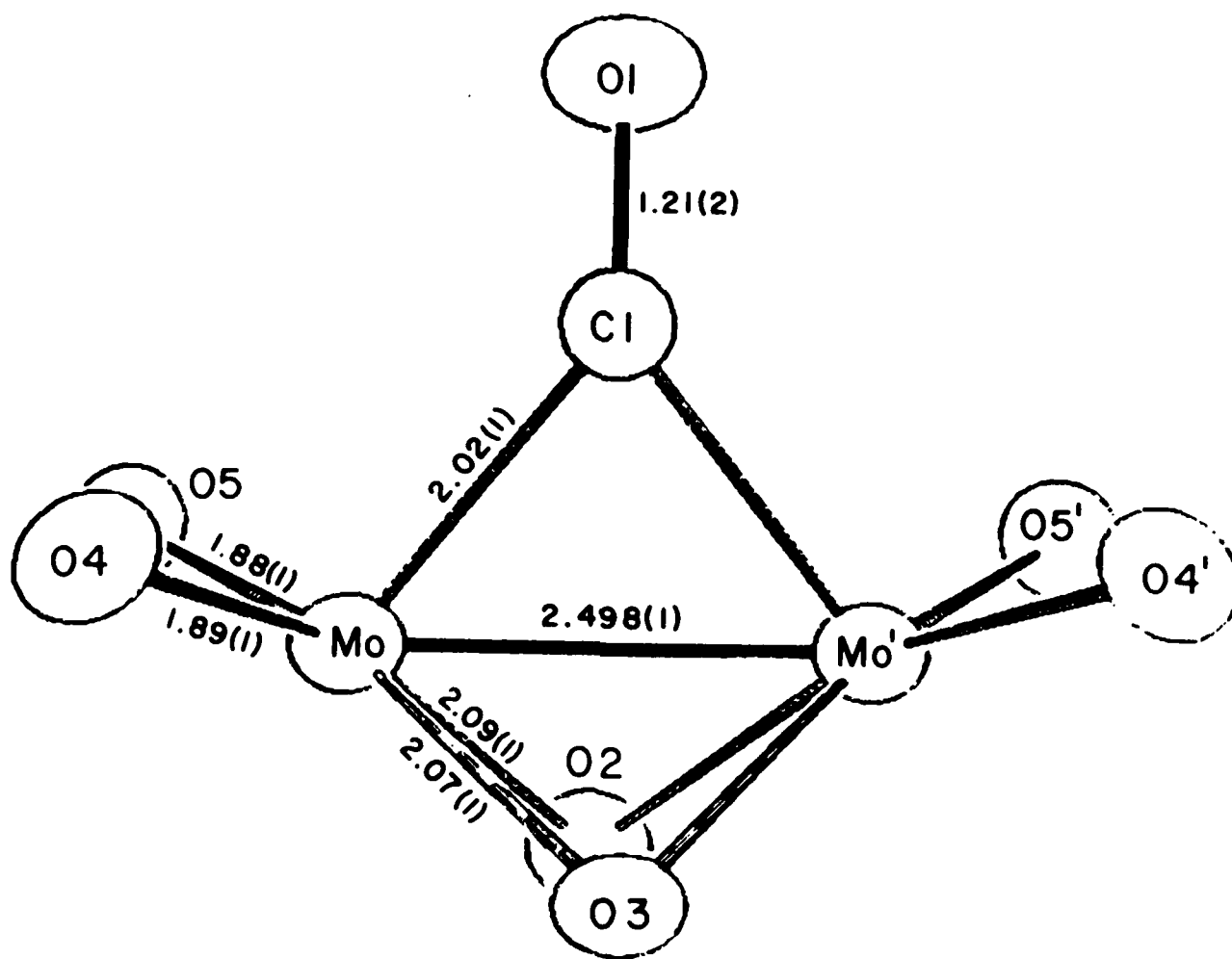




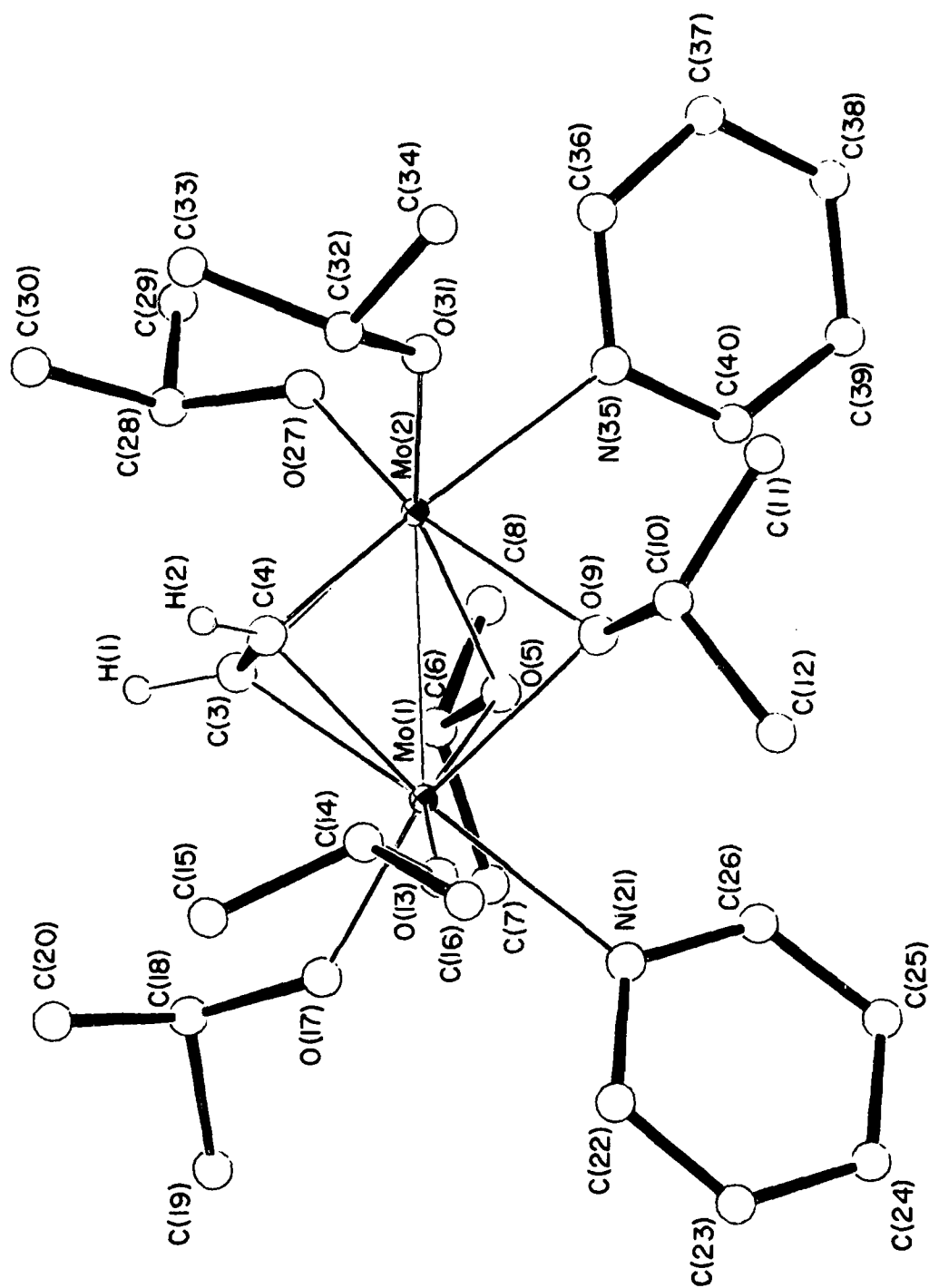


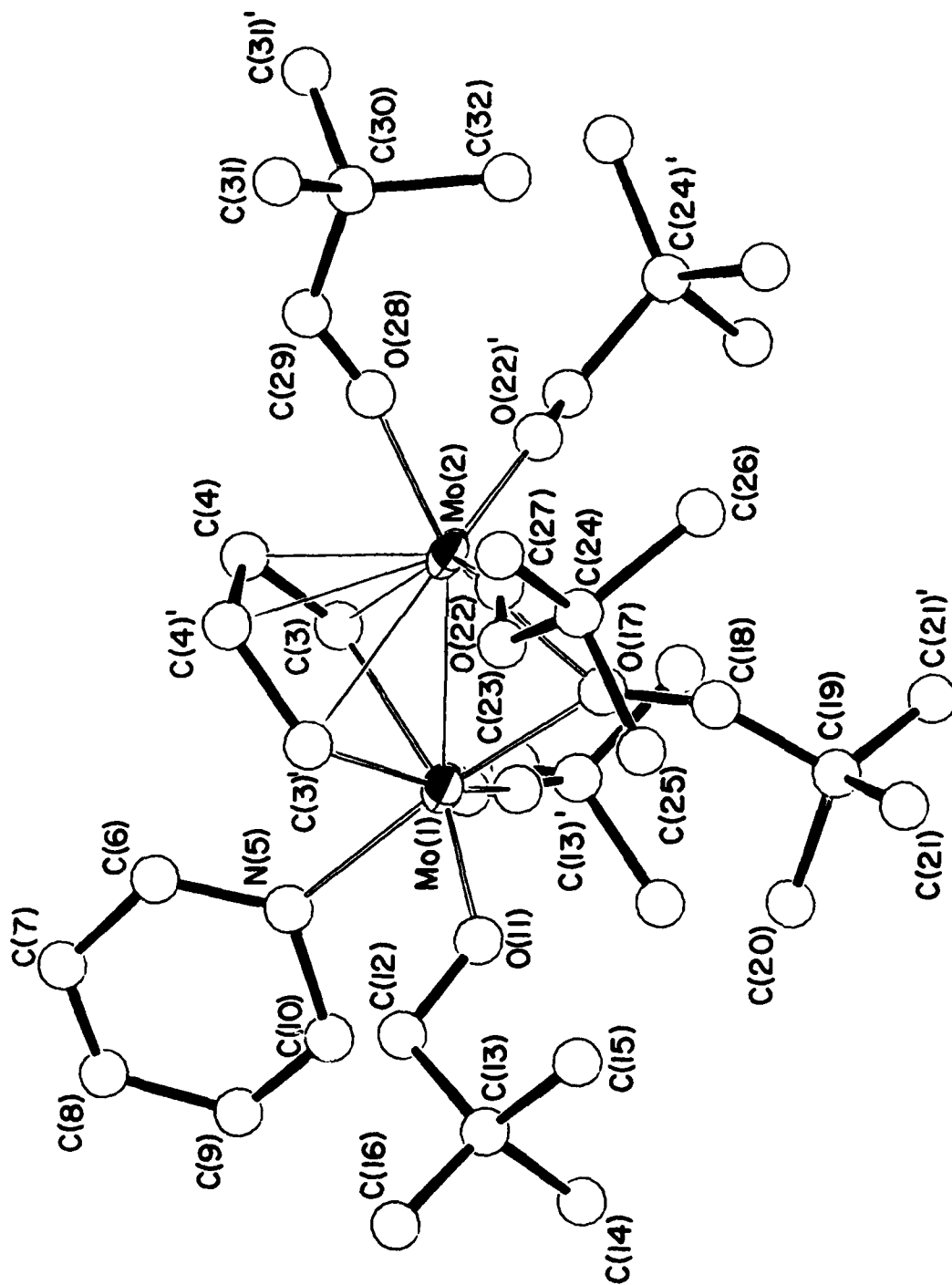






$\text{Mo}_2\text{O}_6(\text{CO})$  Skeleton of  
 $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\text{CO})$





**DAT**  
**FILM**  
**8-8**